

REPORT ON MICROANALYTICAL DETERMINATION OF SULFUR

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Since no previous work had been done toward establishing an official micromethod for sulfur in organic material, this year's study followed the pattern used for the previously reported (1, 2) carbon and hydrogen investigations. Two samples, benzyl-iso-thiourea hydrochloride and sulfanilamide, were sent to each analyst who expressed a willingness to participate and each was asked to analyze the samples by the method currently in use in his laboratory. Detailed questionnaires, one for each of the three combustion methods—catalytic, Carius, and Parr bomb—were sent with the samples, with instructions that the analyst return along with his results the questionnaire that pertained to his method. The collaborator was requested to send all the values obtained, so that a statistical analysis of the data could be made both to compare the different combustion methods and to show the effect of different materials and operations on the results by any one of the three combustion methods.

CATALYTIC COMBUSTION METHOD

Results obtained for sulfur by the catalytic combustion procedure were reported by eleven collaborators. Nine analysts reported thirty-nine values for benzyl-iso-thiourea hydrochloride, and fifty-two values were reported for sulfanilamide by all eleven collaborators. Although the eleven used a catalytic combustion method that was basically the same, there was considerable variation in material and operation in the methods used. Table 1 shows a summary of the analytical data reported as well as a condensation of the information obtained from the completed questionnaires. In this table, n is the number of sulfur values reported by each analyst, \bar{X} is the mean of his data, and s is the standard deviation of his data. The symbols $\bar{\bar{X}}$ and $s_{\bar{x}}$ are used for the mean of all analysts' means, $\bar{\bar{X}}$'s, and the standard deviation of the $\bar{\bar{X}}$'s, respectively. Under the $\bar{\bar{X}}$ column, the values in parentheses are the means of the standard deviations, s , and the means of the values of $\bar{\bar{X}}$ -theory for sulfur.

The two samples used as standards were purified by repeated recrystallization until they were shown to be pure by carbon, hydrogen, and nitrogen analyses in which the official A.O.A.C. micromethods were used. The $\bar{\bar{X}}$'s differ from the theoretical values by only +0.05% for benzyl-iso-thiourea hydrochloride and -0.02% for sulfanilamide. There was also but little difference between the standard deviation of the means, $s_{\bar{x}}$, for the two samples, which were 0.135 and 0.126, respectively.

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TABLE I—Sulfur—catalytic combustion

[illegible]

COLLABORATOR NO.	9	24	28	30	37	50	60	61	45	1	51	\bar{X}	#2
Sample No. 1 Benzyl-isothiourea hydrochloride (15.82% sulfur)	8 15.83 0.179	2 15.84 0.071	2 15.70 0.022	6 15.89 0.168	4 15.93 0.052		8 15.81 0.153	3 16.10 0.205		4 15.70 0.180	2 16.03 0.036	15.87 (0.118)	0.135
Sample No. 2 Sulfanilamide (18.62% sulfur)	8 18.49 0.285	2 18.63 0.247	2 18.49 0.036	8 18.44 0.117	3 18.77 0.149	8 18.51 0.082	8 18.59 0.119	2 18.85 0.031	4 18.58 0.059	4 18.69 0.250	3 18.57 0.087	18.60 (0.113)	0.126
Sample No. 1 Sample No. 2	+0.01 -0.13	+0.02 +0.01	-0.12 -0.13	+0.07 -0.18	+0.11 +0.15	-0.11	-0.01 -0.03	+0.23 +0.23	-0.04	-0.12 +0.07	+0.21 -0.05	(+0.05) (-0.02)	
Burner operation	
Absorbing solution	
Sample weight range	
Burner moved over boat	
Distance burner moved	
Sweeping time	
Total analysis time	
Sulfate determined	
Oxygen flow rate	

* Indicates which of the alternate procedures was used by each collaborator.

The effect of the variations within a method was studied to see whether the data indicated that one procedure would produce more accurate results than the alternate. The variables whose alternate procedures were compared were those listed in Table 1. The data for the two alternate procedures for each variable studied were plotted as shown in Fig. 1.

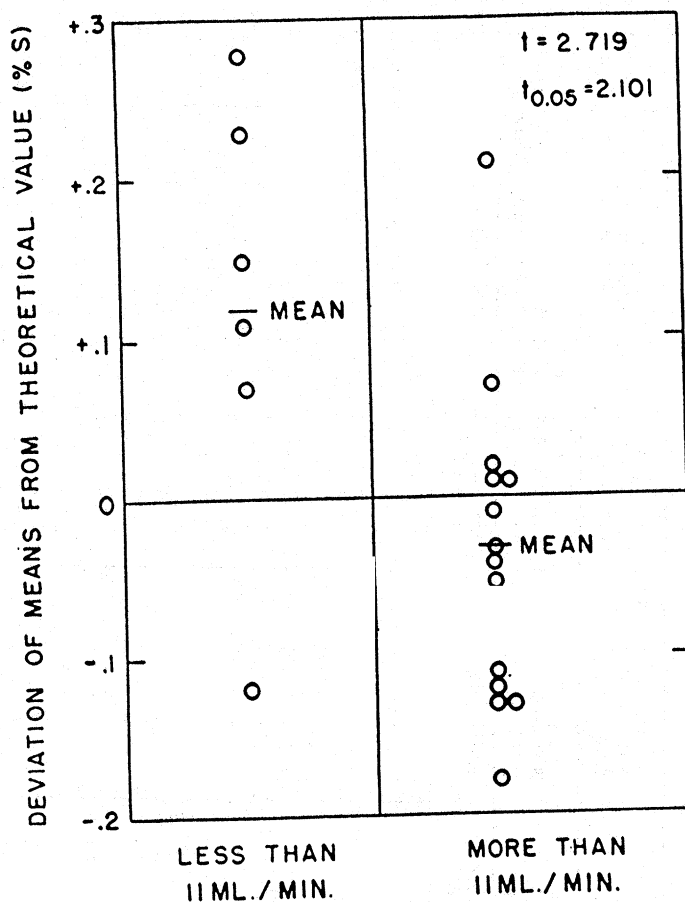


FIG. 1.—Effect of the oxygen flow rate on the determination of sulfur by the catalytic combustion method.

Visual inspection of this plot quickly showed whether there was any marked difference in the data obtained by either of the alternate procedures. When it appeared that a marked visual difference did exist, Student's t value was calculated by the formula

$$t = \frac{\bar{x}}{\sqrt{\frac{n_a n_b (n_a + n_b - 2)}{(n_a + n_b) [\sum (X_a - \bar{X}_a)^2 + \sum (X_b - \bar{X}_b)^2]}}}$$

where $\bar{x} = \bar{X}_a - \bar{X}_b$; n_a and n_b are the number of values in groups a and b , respectively; X_a and X_b are the individual values in the two groups; \bar{X}_a and \bar{X}_b the means of the values for the two groups. If the calculated t value was greater than the critical value, $t_{0.05}$, obtained from a table of Student's t , the difference between the two groups of data was critical at the 95% level, and the procedure whose mean was nearer the theoretical value was considered to be the better. Only two such comparisons

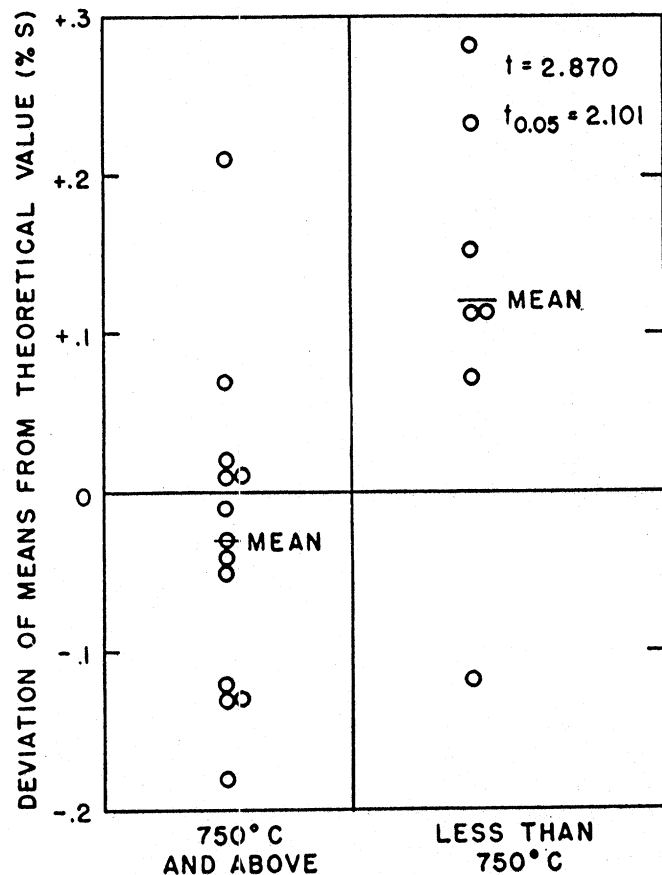


FIG. 2.—Effect of the long furnace temperature on the determination of sulfur by the catalytic combustion method.

had critical t values. These were the oxygen flow rate and the temperature of the long furnace. The data for these comparisons are presented graphically in Figures 1 and 2. The means for the values obtained by using oxygen flow rates below and above 11 ml. per minute were +0.12% and -0.03% from theory, respectively. The calculated t value of 2.719 when compared with a $t_{0.05}$ of 2.101 showed a significant difference between the means. The mean values obtained by using long furnace tem-

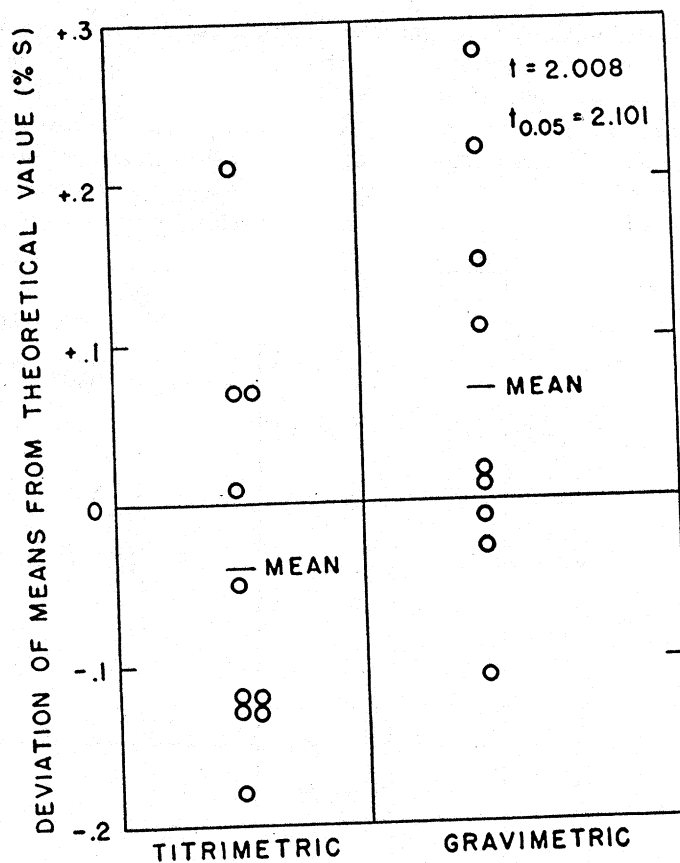


FIG. 3.—Effect of the method of sulfate analysis on the determination of sulfur by the catalytic combustion method.

peratures of 750°C. and over, as opposed to less than 745°C., were -0.03 and $+0.12\%$ from theory; respectively. Comparison of the calculated t value, 2.870, with a $t_{0.05}$ of 2.101 showed the difference between the two means to be significant. It was also noted that the two procedures, slow oxygen flow and low furnace temperature, which might lead to incomplete combustion, were associated with too high sulfur values. One other interesting comparison of results was that obtained by the gravimetric and titrimetric procedures. Although the difference between these two methods was not critical at the 95% level, the t value was so high that the comparison could not be ignored. The data for this comparison, shown in Figure 3, will be referred to later under the discussion of the results obtained by the Carius method.

CARIUS COMBUSTION METHOD

The seventy-nine values furnished by the seven collaborators who used the Carius method were treated in the same manner as those for the cata-

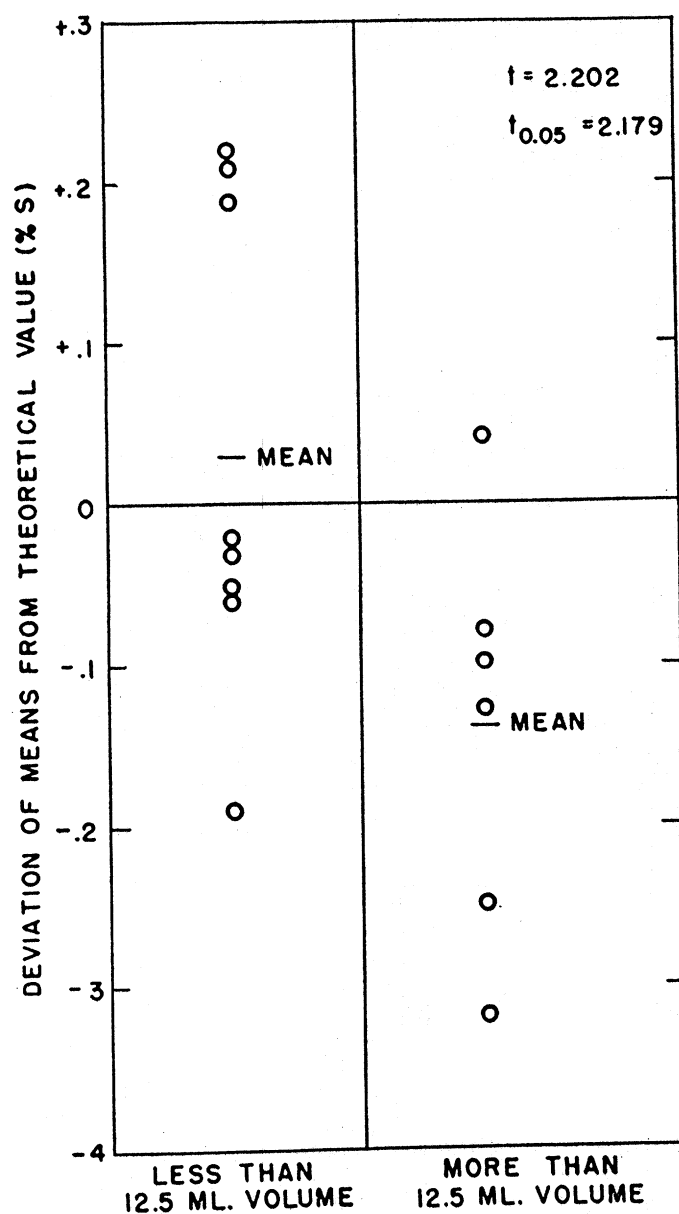


FIG. 4.—Effect of the volume of combustion tube on the determination of sulfur by the Carius combustion method.

lytic combustion method. Table 2 shows a summary of the data and also the variables with alternate procedures, which were studied statistically. The grand mean, \bar{X} , for benzyl-iso-thiourea hydrochloride was 15.79%, which is 0.03% less than the theoretical value of 15.82%; that of sulfanil-

TABLE 2.—Sulfur—Carius combustion

COLLABORATOR NO.			0	17	46	49	50	59	63	\bar{X}	s.d.
Sample No. 1 Benzyl-iso-thiourea hydrochloride (15.82% sulfur)	\bar{X}	\bar{X}	8 15.74 0.064	8 15.75 0.228	6 15.86 0.200	3 15.63 0.127	8 15.76 0.061	3 15.79 0.085	4 16.01 0.097	15.79 (0.123)	0.119
	s	s									
Sample No. 2 Sulfanilamide (18.62% sulfur)	\bar{X}	\bar{X}	8 18.37 0.084	8 18.30 0.498	5 18.49 0.141	3 18.83 0.139	8 18.57 0.174	3 18.60 0.165	4 18.87 0.127	18.57 (0.190)	0.209
	s	s									
Sample No. 1, Sample No. 2,	\bar{X} —theor. value \bar{X} —theor. value		-0.08 -0.25	-0.07 -0.32	+0.04 -0.13	-0.19 +0.21	-0.06 -0.05	-0.03 -0.02	+0.19 +0.22	(-0.03) (-0.05)	
Combustion temperature	300°C. and over Less than 300°		*	*	*	*	*	*	*		
Combustion tube volume (cal. from length and I.D.)	More than 12.5 ml. Less than 12.5 ml.		*	*	*	*	*	*	*		
Sample weight range	2 to 10 mg. More than 10 mg.		*	*	*	*	*	*	*		
Nitric acid	Fuming Concentrated		*	*	*	*	*	*	*		
Volume of nitric acid	0.15 to 3 ml. More than 3 ml.		*	*	*	*	*	*	*		
Reagent added	NaCl or KCl Others		*	*	*	*	*	*	*		
Combustion time	2 to 5.5 hrs. More than 5.5 hrs.		*	*	*	*	*	*	*		
Sulfate determination	Gravimetric Titrimetric		*	*	*	*	*	*	*		

* Indicates which of the alternate procedures was used by each collaborator.

amide was 18.57%, which is 0.05% less than the theoretical value of 18.62%. The standard deviations, s_x , for the sulfur values of the two samples showed a greater difference than those obtained by the catalytic combustion study. The difference, however, was not critical at the 95% level when the F test was applied, $F = (s_x)^2_a / (s_x)^2_b$. Since the data were those of only seven collaborators with a total of fourteen averages, and these data were obtained by using methods where a large number of variables existed, the results of this statistical treatment must be viewed as only indicating a possible trend; they cannot be regarded as conclusive. Nevertheless, it was believed that the statistical treatment of the data was worthwhile and was the best way to obtain any indication of the effect of the variables on the sulfur values. The data obtained under the condition (procedure) of each variable were plotted as shown in Figures 1, 2 and 3, and the t values were calculated for each of these comparisons when the data after visual inspection appeared to be sufficiently different. Only one of the calculated t values was found to exceed the value for $t_{0.05}$, showing that only in one instance a significant difference in the results was obtained by two procedures. This difference was the volume of combustion tubes greater than 12.5 ml versus volumes less than 12.5 ml. The volumes were calculated from the length and inside diameter of the tubes used. Figure 4 shows the data for this comparison. It can be seen that tubes with volumes greater than 12.5 ml lead to low results, since the mean value for the data obtained with the larger tubes was 0.14% less than the theoretical value, whereas with the smaller tube the mean was only 0.03% higher than the theoretical value.

The comparison of gravimetric versus titrimetric methods for the sulfate determination gave a t value only slightly less than the critical value. Figure 5 shows the data for this comparison. For a better statistical comparison of the data by gravimetric and titrimetric procedures for sulfate analysis, all the data obtained by the catalytic combustion and the Carius combustion methods were combined. Figure 6 shows the combined data. The new t value, 2.978, compared with $t_{0.05}$ of 2.037 showed that the difference between the data for the two methods is highly significant. Although the difference is significant, there is but little choice between the gravimetric and the titrimetric methods based on the deviation of the mean sulfur value from the theoretical sulfur value, since the deviation of the gravimetric values was +0.08% and that of the titrimetric values was -0.06%. The gravimetric method gave high results, probably because of adsorption and co-precipitation with the barium sulfate precipitate. The results of the titrimetric method may be lower because the true stoichiometric point may not be reached, owing to the slowness of the indicator in reaching equilibrium when the titration nears the end point.



FIG. 5.—Effect of the method of sulfate determination on the determination of sulfur by the Carius combustion method.

PARR BOMB COMBUSTION

Seven collaborators reported fifty-four sulfur values, but no comparison of procedures using the *t* test was feasible because of the similarity of most of the procedures. Table 3 presents a summary of the data reported. The

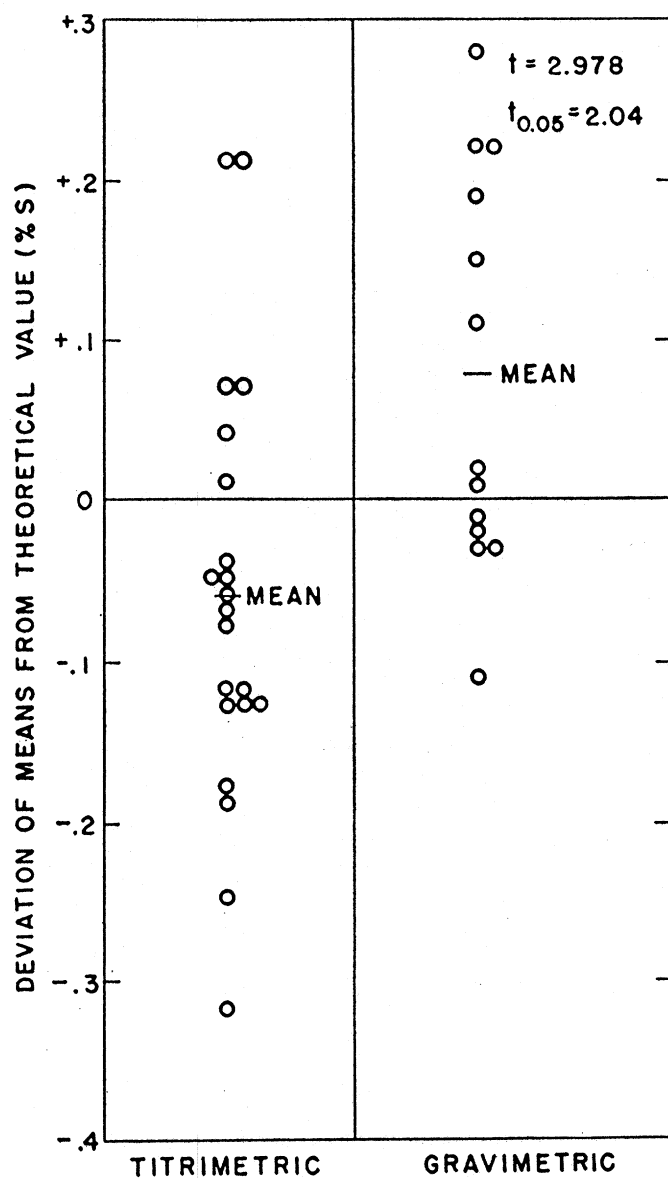


FIG. 6.—Effect of the method of sulfate analysis on the determination of sulfur. (Combined catalytic and Carius combustion data).

grand mean, $\bar{\bar{X}}$, of the individual means, \bar{X} 's, for the sulfur values for the two compounds were only +0.06 and -0.03% from the theoretical values, but the standard deviations of the means $s_{\bar{x}}$ were 0.391 and 0.176. This difference was found to be critical at the 95% level by applying the F test, $F = (s_{\bar{x}})^2_a / (s_{\bar{x}})^2_b$. F calculated was 4.93, and $F_{0.05}$ was 4.28.

TABLE 3.—Sulfur—Parr bomb combustion

COLLABORATOR NO.		8	15	24	29	44	65	23	\bar{X}	sd
Sample No. 1 Benzyl-iso-thiourea hydrochloride (15.82% sulfur)	n		6	1	4	4	4	4		
	\bar{X} s		16.50 0.488	15.73 —	15.83 0.101	15.44 0.211	15.98 0.097	15.79 0.174	15.88 (0.224)	0.301
Sample No. 2 Sulfenamide (18.62% sulfur)	n	2	8	3	4	4	5	4		
	\bar{X} s	18.53 0.318	18.60 1.470	18.73 0.026	18.70 0.116	18.24 0.059	18.64 0.060	18.72 0.109	18.59 (0.342)	0.176
Sample No. 1 Sample No. 2	\bar{X} —theor. value		+0.70	-0.09	+0.01	-0.38	+0.16	-0.03	(+0.06)	
	\bar{X} —theor. value	-0.09	-0.02	+0.11	+0.08	-0.38	+0.02	+0.10	(-0.03)	

Thus far, only comparisons have been made of data obtained by alternate procedures for a variable in one of the three methods. To determine whether any one of the methods gave more accurate or precise results than the others, the t and F tests were applied to the three possible pairs of data, that is, Carius versus Parr, Carius versus catalytic, and Parr versus catalytic combustion. The data for sample No. 1 and sample No. 2 were compared separately, and the combined data for the two samples were compared. No critical t values were obtained, so there were no significant differences in the means, \bar{X} 's, obtained by the three methods. Neither were there any critical F values when the one high sulfur value of 16.5 for benzyl-iso-thiourea hydrochloride by the Parr bomb method was discarded. When this value was included, critical F values were obtained when the data for sample No. 1 by the Parr method were compared with those for the other two. Thus, when this single value was included in the calculations, the results by the Parr method for benzyl-iso-thiourea hydrochloride were less precise than those by the other two methods.

Collaborators on sulfur analysis were:

Alicino, J. F., Squibb Institute for Medical Research; Bier, Milan, Fordham University; Bronk, L. R., General Electric Company; Brown, L. E., Southern Regional Research Laboratory; Brown, Wm. L., Eli Lilly and Company; Browning, B. L., The Institute of Paper Chemistry; Brunner, A. H., Ansco; Dorfman, Louis, Ciba Pharmaceutical Company; Dutton, C. D., Picatinny Arsenal; Feldman, J. R., General Foods Corporation; Jones, G. A., E. I. duPont de Nemours and Company; Ketchum, D. F., Eastman Kodak Company; Koch, C. W., University of California; Lohr, L. J., General Aniline and Film Corporation; Ogg, C. L., Eastern Regional Research Laboratory; Rush, C. A., Edgewood Arsenal; Savacool, Ruth, Smith, Kline and French; Scafe, E. T., Sacony Vacuum Oil Company; Steyermark, Al, Hoffmann-La Roche, Inc.; Streeter, K. B., Sharpe and Dohme; Sundberg, A. E., Calco-American Cyanamide Company; Throckmorton, W. H., Tennessee Eastman Corporation; Van Etten, C. H., Northern Regional Research Laboratory.

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